

*Full Length Research Paper*

# Preparation, characterization and microbiological studies of $\text{Cr}^{+3}$ , $\text{Mn}^{+2}$ , $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ , $\text{Cu}^{+2}$ , $\text{Zn}^{+2}$ and $\text{Cd}^{+2}$ chelates of schiffs base derived from vanillin and anthranilic acid

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**New chelates of schiffs base derived from vanillin and anthranilic acid with d-block elements such as  $\text{Cr}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  have been synthesized and investigated. Their structures were determined on the basis of the elemental analysis, infrared spectroscopy, electronic spectroscopy, thermo gravimetric analyses and electron spin resonance spectroscopy. Molar conductivity measured revealed the 1:1 electrolytic nature for  $\text{Cr}^{+3}$  complexes and non electrolytic for  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$ . On the basis of the studies, the coordination sites were proven to come through the nitrogen atom of azomethine and the hydroxyl group of the carboxyl group of anthranilic acid.**

**Key words:** Metal complexes, anthranilic acid, vanillin, chelates.

## INTRODUCTION

Complexes of schiffs bases are of great importance due to their biological, pharmaceutical, clinical and analytical applications (Shrivastava et al., 2004; Cenicerros-Gomez et al., 2002), whereas  $\text{Cr}^{+3}$  chelates of schiffs base derived from vanillin and anthranilic acid have been reported in the presence of pyridine as one of the ligand in a octahedral complex (Dubey et al., 2006). A thorough knowledge of the coordination chemistry of schiffs base derived from vanillin and anthranilic acid with metals such as  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  will be of much interest in elucidating the structure, reactivity and microbiological study of the complexes.

## EXPERIMENTAL

### Materials

All the chemicals and solvents were of AR grade. Metal salts were purchased from Merck and Loba chemie, Mumbai, India. Vanillin and anthranilic acid were purchased from Loba chemie, Mumbai,

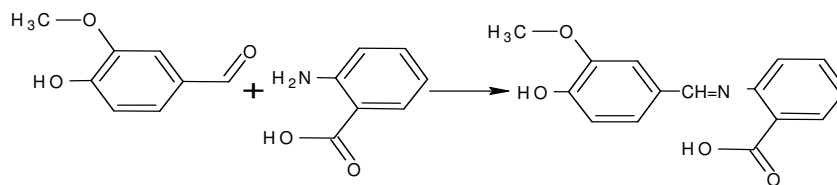
India, while ethanol, methanol and the solvents were dried by the standard procedures (Brian et al., 1996; Argarego and Perrin, 1997). The elemental analyses were performed at Central Electro Chemical Research Institute (CECRI), India, using vario EL elemental analyzer. IR spectroscopy analyses were recorded on Shimadzu FTIR 8400S spectrometer in  $4000 - 200 \text{ cm}^{-1}$  range using KBr pellet, while the UV-Visible spectra were recorded on a Shimadzu UV spectrometer in the wave length range of 200 - 800 nm.

The thermal analyses were recorded on a universal V4.3A TA instrument from CECRI, India, while the ESR (erythrocyte sedimentation rate) spectral analyses were recorded on a Bruker instrument at 300 and 77 K from CECRI. The molar conductance was measured on ELICO-CM180 using DMSO (Dimethyl sulfoxide) as the solvent at room temperature, whereas the antibacterial activity was determined with the disc diffusion method. Subsequently, stock solutions were prepared by dissolving the compounds, while DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC).

### Synthesis of the schiffs' base

The schiffs base from vanillin and anthranilic acid was prepared by adding 4.278 gm (0.02 mol) of vanillin in 25 ml ethanol and 3.856 gm (0.02 mol) of anthranilic acid in 25 ml ethanol with constant stirring for ten minutes. The contents were refluxed on a water bath

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**Figure 1.** Reaction showing formation of schiffs base ligand.

for 4 - 5 h. Subsequently, they were cooled and poured into a crushed ice. The oily liquid, over the water, is allowed to stay aside for some time (Brian et al., 1996).

### Preparation

While crystals of the schiffs base starts to appear. The resulting solid product is washed with distilled water and ethanol several times and is then recrystallized with ethanol. The scheme of preparation is shown in Figure 1. The synthesis and structural analyses were carried out according to the method cited earlier (Dubey et al., 2006; Vogel, 1978).

### Synthesis of complexes

The 1:2 complexes of the metal and ligand are prepared by taking 0.04 mol (10.18 gm) schiffs base in 50 ml of ethanol. The corresponding hydrated metal salts of  $\text{Cr}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  of 0.02 mol was dissolved in 50 ml hot ethanol. The hot ethanol solution of metal salt was slowly added to the hot alcoholic solution of the ligand. The resulting mixture was refluxed for 4 - 5 h, while few drops of sodium hydroxide were added in drops to act as catalyst for the reaction. The colored precipitate ( $\text{Cr}^{+3}$ -green,  $\text{Mn}^{+2}$ -cream,  $\text{Co}^{+2}$ -pink,  $\text{Ni}^{+2}$ -green,  $\text{Cu}^{+2}$ -green,  $\text{Zn}^{+2}$ -cream white and  $\text{Cd}^{+2}$ -pink) was separated by filtration and washed with distilled water, hot ethanol and ether.

### Antibacterial activity

The antibacterial activity was determined with the disc diffusion method. Stock solutions were prepared by dissolving the compounds, while DMSO and serial dilutions of the compounds were prepared in a sterile distilled water to determine the minimum inhibition concentration (MIC). However, the nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Fifty micro litres of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature ( $29 \pm 2^\circ\text{C}$ ) for 30 - 36 h. The diameter of the inhibition zones was measured in millimeters.

## RESULTS

The analytical data for the complexes together with their physical properties are summarized in Table 1. The conductance values of the chelates support the 1:1 electrolytic nature for  $\text{Cr}^{+3}$  complexes and non electrolytic

nature for  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  complexes.

### Infrared spectra and mode of bonding

The diagnostic IR frequencies of the ligand and its complexes are compiled in Table 2. The infrared spectrum of the free ligand is compared with that of the complexes to determine the coordination sites that may have been involved in the chelation.

### Electronic spectral analyses

The UV- spectrum of Chromium (III) complex shows three peaks at 742 ( $13477\text{ cm}^{-1}$ ), 670 ( $14925\text{ cm}^{-1}$ ) and 290 nm ( $34482\text{ cm}^{-1}$ ) respectively. The peak at 742 ( $13477\text{ cm}^{-1}$ ), 670 ( $14925\text{ cm}^{-1}$ ) and 290 nm ( $34482\text{ cm}^{-1}$ ) corresponds to the  $3A_{2g} \rightarrow 3T_{2g}$ ,  $3A_{2g} \rightarrow 3T_{1g}$  (F) and  $3A_{2g} \rightarrow 3T_{1g}$  (P) electronic transition, respectively. The electronic transitions observed for the Cr (III) complexes suggest the octahedral geometry for the complex (Table 3). The Orgel diagram for the  $d^3$  configuration of  $\text{Mn}^{+2}$  shows the three bands at 423.50 ( $23612\text{ cm}^{-1}$ ), 392 ( $25510\text{ cm}^{-1}$ ) and 327 nm ( $30581\text{ cm}^{-1}$ ) assigned for  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (S),  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) and  ${}^6A_{1g} \rightarrow {}^4A_{1g}$ , respectively. Thus, the  $\text{Mn}^{+2}$  complexes have octahedral geometry. Three peaks are predicted for cobalt in their electronic spectra, namely,  ${}^4T_{2g} \rightarrow {}^4T_{2g} v_1$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g} v_2$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}$  (P)  $v_3$  found at 604 ( $16556\text{ cm}^{-1}$ ), 352 ( $28409\text{ cm}^{-1}$ ) and 342 nm ( $29239\text{ cm}^{-1}$ ), respectively for the cobalt complex. This shows the presence of an octahedral structure in cobalt complex. Nickel (II) has a ( $d^8$ ) and its absorption is found at 648 ( $15432\text{ cm}^{-1}$ ), 349 ( $28653\text{ cm}^{-1}$ ) and 338 nm ( $29585\text{ cm}^{-1}$ ) respectively for the nickel complex. Based on the Orgel diagram, the first peak at 648 nm is assigned to the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ , while the second at 349 nm to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and the third at 338 nm to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) transition respectively. This confirms the presence of an octahedral geometry for the nickel complex. Copper (II) has a ( $d^9$ ) configuration having the following absorption found at 757.5 nm ( $13200\text{ cm}^{-1}$ ) for the  ${}^2A_{1g} \rightarrow {}^2B_{1g}$  ( $d_z^2 \rightarrow d_{x^2-y^2}$ )  $v_1$ , 533.9 nm ( $18730\text{ cm}^{-1}$ ) for  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ )  $v_2$  and 415 nm ( $24096\text{ cm}^{-1}$ ) for the  ${}^2E_g \rightarrow {}^2B_{1g}$  ( $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ )  $v_3$ , respectively for the copper complex.

**Table 1.** Analytical data and physical properties of the synthesized complexes.

Compound (Empirical formula)	Elemental analyses found (Calcd), %				Colour	$\Lambda_m$ (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
	C	H	N	Metal		
[Cr <sup>+3</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> ClCr <sup>+3</sup>	53.32 (54.26)	4.62 (4.52)	4.08 (4.22)	7.80 (7.83)	Green	46.48
[Mn <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> Mn <sup>+2</sup>	55.05 (57.05)	4.542 (4.754)	4.382 (4.438)	8.80 (8.707)	Cream	1.4
[Co <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> ClCo <sup>+2</sup>	55.9 (56.8)	4.68 (4.74)	4.38 (4.42)	8.80 (8.51)	Pink	1.4
[Ni <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> Ni <sup>+2</sup>	55.9 (56.8)	4.68 (4.74)	4.38 (4.42)	8.80 (8.67)	Green	1.88
[Cu <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> ClCu <sup>+2</sup>	55.2 (56.3)	4.63 (4.69)	4.348 (4.378)	9.936 (9.8)	Green	1.88
[Zn <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> ClZn <sup>+2</sup>	55.18 (56.13)	4.281 (4.366)	4.262 (4.366)	10.088 (10.19)	Cream white	1.56
[Cd <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>10</sub> ClCd <sup>+2</sup>	51.93 (52.29)	4.031 (4.067)	4.028 (4.067)	16.07 (16.33)	Pink	1.46

**Table 2.** Characteristic infrared absorption frequencies in (cm<sup>-1</sup>) of ligand (L) and complexes.

No.	Compound	$\nu$ (OH) water	$\nu$ (OH) phenolic	$\nu$ cm <sup>-1</sup> C = O	$\nu$ cm <sup>-1</sup> C = N	$\nu$ cm <sup>-1</sup> COO <sup>-</sup>	$\nu$ M-O coordinated water	$\nu$ M-O
1	C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub>		3239	1668	1585	1481		
2	[Cr <sup>+3</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl	3274	3122	1599	1552	1460	871	707
3	[Mn <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3304	3144	1593	1543	1455	864	715
5	[Co <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3307	3138	1593	1540	1458	869	715
6	[Ni <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3303	3125	1597	1540	1457	870	714
7	[Cu <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3443	3122	1598	1553	1459	870	711
8	[Zn <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3299	3131	1594	1543	1457	867	716
9	[Cd <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3289	3140	1591	1535	1449	861	713

**Table 3.** UV-visible spectral data of the compounds.

S/No.	Complex	$\Lambda$ max cm <sup>-1</sup>	10Dq cm <sup>-1</sup>	B cm <sup>-1</sup>	$\beta$	Geometry
1	[Cr <sup>+3</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl	13477, 14925 and 34482 cm <sup>-1</sup>	13477	556.2	0.54	Octahedral
2	[Co <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	16556, 28409 and 29239 cm <sup>-1</sup>	11853	532	0.475	Octahedral
3	[Ni <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	15432, 28653 and 29585 cm <sup>-1</sup>	15432	796	0.737	Octahedral

Based on the Orgel diagram, the peak at 790 nm (12650 cm<sup>-1</sup>) is assigned for the <sup>2</sup>E<sub>g</sub> → 2T<sub>2g</sub> transition. This confirms the presence of octahedral geometry in the copper complex. Zinc (II) shows absorption at 360 nm (27777 cm<sup>-1</sup>) for the ligand metal charge transfer

transition and this confirms the presence of an octahedral geometry in the zinc complex. Cadmium (II) shows absorption at 350 nm (28571 cm<sup>-1</sup>) for the ligand metal charge transfer transition and this confirms the presence of an octahedral geometry in the cadmium complex.

**Table 4.** Thermo gravimetric analyses of complexes.

S/No.	Compound	Temp. range (°C)	Stage	Weight loss (%)	
				Found	Calculated
1	[Cr <sup>+3</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl	122.21 - 193.47	I	5.08	5.4
		193.47 - 634.21	II	82.81	83.17
		Above 634.21	-	11.31	11.42
2	[Mn <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	105.97 - 342	I	5.22	5.71
		342.00 - 547	II	82.67	82.73
		Above 547	-	12.11	11.09
3	[Ni <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	207.72 - 368	I	6.9	5.84
		368 - 650.23	II	43.56	44.74
		Above 650.23	-	12.04	12.03
4	[Cu <sup>+2</sup> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	55.61	I	2.84	2.81
		55.61 - 152.12	II	16.68	16.57
		152.12 - 407.67	III	69.38	68.18
		Above 407.67	-	11.10	12.35

### Thermal analyses

Thermo gravimetric analyses (TGA) of the complexes are used (Gehad et al., 2005; Soliman and Linert, 1999) to get the (i) information on the water of hydration if present in the coordination sphere of the central metal ion, (ii) the scheme of thermal decomposition of the complexes and (iii) to decide about the thermal stability of the new complexes. In the current study, heating at the rate of 10 °C per minute was done up to the temperature of 1000 °C (Table 4).

### ESR analyses

The ESR spectra of copper complex provide important information in studying the metal ion, while the ESR spectra of the Cu (II) complex are recorded at liquid nitrogen temperature (77 K) and room temperature (300 K). The spectrum of copper complex has a single intense absorption band in the high field region and its molecule is isotropic due to the tumbling motion of the molecule. When the complex is frozen to liquid nitrogen temperature, four well resolved peaks with low field region are obtained. This shows the presence of an octahedral geometry for the copper complex.

### Antibacterial activity

The antibacterial activity was determined with the disc diffusion method (Raman et al., 2004; Shirin and Mukherjee, 1992). Stock solutions were prepared by dissolving the compounds, while DMSO and serial dilutions of the compounds were prepared in sterile distilled water

to determine the minimum inhibition concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader.

Subsequently, fifty microlitres of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature (29±2 °C) for 30 - 36 h. The diameter of the inhibition zones was measured in millimeters. The synthesized ligand and complexes were tested for their antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. Table 5 shows that Zn<sup>+2</sup> and Cd<sup>+2</sup> complexes show good antibacterial activity against the strain of bacteria taken under study.

## DISCUSSION

### Infrared spectra and mode of bonding

It is noted that the ν (OH) water is absent in the spectrum of the ligand but is present in the complexes. This shows the presence of hydration water in the complexes. This is supported by the presence of the ν M-O peaks noticed in the complexes and absent in the ligand. The phenolic ν OH stretching does not undergo any change in the spectrum; hence, the phenolic OH group does not

**Table 5.** Antibacterial activity data for the ligand and their metal complexes.

S/No.	Compound	<i>S. aureus</i>	<i>E. coli</i>	Inference on anti bacterial activity
1	C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub>	4	3	+
2	[Cr <sup>+3</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl	6	5	+
3	[Mn <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	7	6	+
5	[Co <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	-	-	No effect
6	[Ni <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	4	3	+
7	[Cu <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	-	-	No effect
8	[Zn <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	18	17	+++++
9	[Cd <sup>+2</sup> L <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	10	10	++

participate in the bond formation with metals. The frequency corresponding to the carboxylate hydrogen  $\nu$  COOH stretching is found to be broad on the region (2586 cm<sup>-1</sup>) in the ligand. This broad band is absent in all the complexes, showing the participation of carboxylate anion group in chelation. The frequency corresponding to the  $\nu$  (C=O) stretching in the region (1668 cm<sup>-1</sup>) that is in the ligand is shifted to a lower frequency in the complexes. The frequency corresponding to (C = N) at 1585 cm<sup>-1</sup> also shifts to lower frequency in the complexes and the frequency of  $\nu$  (COO) present in the ligand 1481cm<sup>-1</sup> is respectively shifted (Gehad et al., 2005; Kalagouda et al., 2007) to the lower wave number.

### IR spectrum

Thus, it is concluded from the IR spectrum that the metals are participating in the bond formation through the azomethine C = N group and the carboxylate COO<sup>-</sup> anion of the acid group (Chiswell et al., 1964; Liu et al., 2006; Maihub et al., 1982; Mehrotra and Singh, 1984; Mukerrem and Esin, 2007; Nair and Joseyphus, 2007; Nakamoto, 1964; Renehan et al., 2005; Water and Freiser, 1952; Wu and Yen 1993).

### Electronic spectral analyses

The ligand shows absorption peaks in the UV region corresponding to the  $\pi \rightarrow \pi^*$  and  $n - \pi^*$  transitions. Various ligand field parameters have been evaluated for the Cr (III) complex. Copper (II) has a (d<sup>9</sup>) configuration having the following absorption found at 757.5 nm (13200 cm<sup>-1</sup>) for the <sup>2</sup>A<sub>1g</sub> → <sup>2</sup>B<sub>1g</sub> (d<sub>z</sub><sup>2</sup> → d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)  $\nu_1$ , 533.9 nm (18730cm<sup>-1</sup>) for the <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>B<sub>1g</sub> (d<sub>xy</sub> → d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)  $\nu_2$  and 415 nm (24096 cm<sup>-1</sup>) for the <sup>2</sup>E<sub>g</sub> → <sup>2</sup>B<sub>1g</sub> (d<sub>xz</sub>, d<sub>yz</sub> → d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)  $\nu_3$ , respectively for the copper complex. The spectra are typical of Cu (II) complexes with an elongated tetragonal (Sulekh et al., 2009). The value of the first spin allowed transition ( $\nu_1$ ) at approximately 13477cm<sup>-1</sup>, which is directly taken as 10Dq. The value of Racah parameter (B) can be evaluated by the equation of underhill and

Billing (Dubey et al., 2006; Dubey et al., 2005; Krishnapillai et al., 2005)  $B = (\nu_3 + \nu_2 - 30Dq)/15$ . The observed value of 556.2 of the Racah interelectronic repulsion parameter (B') was compared to the free Cr<sup>+3</sup> ion (1030 cm<sup>-1</sup>), which indicates a considerable covalent character of the metal-ligand bonds with covalency factor  $\beta = 0.54$ . Similarly, the ligand parameters for the other metals were calculated.

### UV spectroscopy

Thus, based on the UV-visible spectroscopy, it is found that metals form complexes with the prepared schiffs base ligand with octahedral geometry (Cezar and Angela, 2000; Dubey et al., 2005a; Dubey et al., 2005b; Dunn, 1960; Figgis, 1976; Geary, 1971; Selvin et al., 2006).

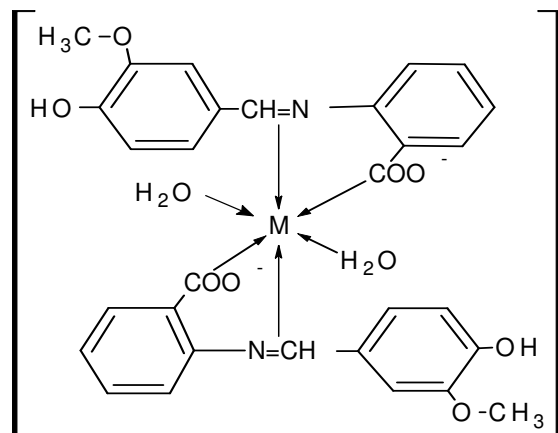
### Thermal analyses

The TGA analyses show the presence of octahedral geometry for the complexes. Two molecules of water are present in the coordination sphere that is lost in stage I. In stage II, the complex decomposes and in stage III, the residue is formed. However, the calculated and observed values are almost the same.

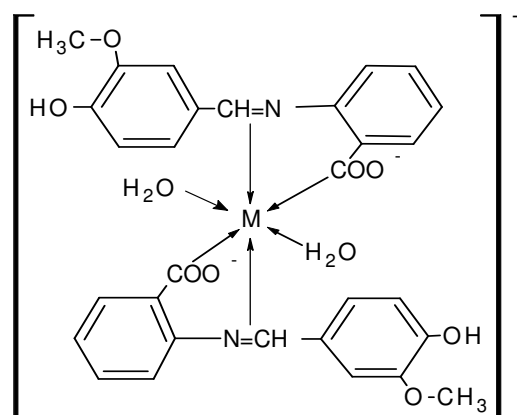
### ESR analyses

The four well resolved peaks in the low field region (Sulekh et al., 2009) correspond to g<sub>||</sub> (2.288) and g<sub>⊥</sub> (2.0428). The trend g<sub>||</sub> (2.288) > g<sub>⊥</sub> (2.0428) > g<sub>e</sub> (2.0023) observed for the copper complex suggests that the unpaired electron is localized in the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital of the copper ion. The fact that the unpaired electron lies predominantly in the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital is also supported by the value of the exchange interaction G estimated from expression

$$G = (g_{||} - 2.0023) / (g_{\perp} - 2.0023) \quad (1)$$



**Figure 2.** . Structure of  $Mn^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  and  $Cd^{+2}$



**Figure 3.** Structure of  $Cr^{+3}$  complex.

If  $G > 4.0$ , the local axes are aligned parallel or slightly misaligned. If  $G < 4.0$ , significant exchange coupling is present and the misalignment is appreciable. The observed value of the exchange interaction parameter for the Cu (II) complex ( $G = 7.054$ ) suggests that the unpaired electron is present in the  $d_{x^2-y^2}$  orbital. However, the spin orbit coupling constant, which is

$\lambda$  (value :  $-25595 \text{ cm}^{-1}$ ) was calculated using the relation,

$$g_{av} = 1/3 (g_{\parallel} + 2 g_{\perp}) \text{ and } g_{av} = 2 (1 - 2 \lambda / 10 Dq) \quad (2)$$

is less than that for the free Cu (II) ion,  $-12019 \text{ cm}^{-1}$ , which also supports the covalent character of the M-L bond in the complex. The covalency parameter,  $\alpha^2$ , was calculated using the following equation:

$$\alpha^2 (\text{Cu}) = A_{\parallel} / P + (g_{\parallel} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.004$$

$$\alpha^2 (\text{Cu}) = (A_{\parallel} / 0.036) + (g_{\parallel} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.004 \quad (3)$$

The  $\alpha^2$  (0.7214) value for the complex supports its covalent nature of the bonding. Hathway (Sulekh et al., 2009) pointed out that for the pure  $\sigma$  - bonding,  $K_{\parallel} > K_{\perp} \approx 0.77$ ; for the in-plane  $\pi$ - bonding,  $K_{\parallel} < K_{\perp}$ ; while for the out-of-plane  $\pi$ - bonding,  $K_{\perp} < K_{\parallel}$ . However, the following simplified expressions were used to calculate  $K_{\parallel}$  and  $K_{\perp}$ .

$$K_{\parallel} = (g_{\parallel} - 2.0023 / 8 \times \lambda_0) \times d - d \text{ transition} \quad (4)$$

$$K_{\perp} = (g_{\perp} - 2.0023 / 2 \times \lambda_0) \times d - d \text{ transition} \quad (5)$$

The observed  $K_{\parallel}$  (0.7231)  $>$   $K_{\perp}$  (0.4532) relation indicates

the absence of significant in- plane  $\pi$ - bonding. The molar conductance of the complexes reveals the presence of chloride ions outside the coordination sphere in chromium and iron complexes. In the complexes of  $Mn^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  and  $Cd^{+2}$ , the primary valency of the metals are satisfied within the coordination sphere due to the coordination with the carboxyl ate groups of the ligand.

### Antibacterial activity

The antibacterial property of the ligands was compared to the complexes and as a result, the  $Zn^{+2}$  and  $Cd^{+2}$  complexes show good antibacterial activity against the strain of bacteria taken under study when compared to the ligand and other metal complexes taken for the study.

### Conclusion

In this paper, we have reported the co-ordination chemistry of complexes derived from schiffs' base ligand and obtained from the reaction of vanillin and anthranilic acid with metals such as  $Cr^{+3}$ ,  $Mn^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  and  $Cd^{+2}$ . Both the structures of the ligand (Shrivastava et al., 2004) and complexes were confirmed by elemental analyses, IR, molar conductance, UV-Visible spectroscopy, thermo gravimetric analyses and ESR spectroscopic analyses.

The schiffs base coordinates were gotten through its azomethine nitrogen and the carboxyl ate group to the central metal atom, while the schiffs base behaves as a bidentate ligand. The molar conductance measurements suggest the presence of chloride ion outside the coordination sphere for  $Cr^{+3}$  as shown in Figure 3. However, the metals,  $Mn^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  and  $Cd^{+2}$ , form 1:2 complexes with the schiffs base ligand as shown in Figure 2.

Additional comments: The details on the study of

antibacterial study can be obtained from the following website: [http://www.sciencebuddies.org/science-fair-projects/project\\_ideas/MicroBio\\_p014.shtml](http://www.sciencebuddies.org/science-fair-projects/project_ideas/MicroBio_p014.shtml).

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